



Polymer electrolyte membranes based on poly(arylene ether)s with flexible disulfophenyl pendant



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HIGHLIGHTS

- Poly(arylene ether)s containing flexible disulfonic acid pendant was synthesized.
- The I-50 exhibited comparable conductivity to Nafion 117 and lower swelling ratio.
- Disulfonic acid side chain I-x was better than SP-90 with similar IEC value.

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ABSTRACT

New difluoride monomer containing a biphenyl pendant group is designed and synthesized for preparing side chain style polyelectrolyte. As a result, a novel poly(arylene ether)s containing flexible disulfonic acid pendant are obtained by a two-step synthetic procedure. First, poly(arylene ether)s with electron-rich side groups as polymer precursor (P-x) are prepared from designed difluoride monomer, 4,4'-difluorobenzophenone (DFDPK), and 4,4'-(hexafluoroisopropylidene)diphenol (6FBPA) by nucleophilic polycondensation. Then objective sulfonated polymers (I-x) are obtained from P-x and chlorosulfonic acid by sulfonation reaction. Tough, flexible, and transparent membranes having high mechanical strength are obtained by solution casting of I-x polymer. The membrane I-x exhibits high proton conductivity and good dimensional stability, which attributes their special side chain style structure. For example, I-50 membrane ($\text{IEC} = 1.32 \text{ meq. g}^{-1}$) shows low swelling of 8.1% and comparable conductivity with Nafion 117 at 80 °C. Suitable morphology is observed in I-x membranes by SAXS test, which may explain that I-x possess perfect overall properties.

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1. Introduction

Proton exchange membranes fuel cells (PEMFCs), which convert chemical energy directly into electrical work, are regarded as a promising candidate for power sources owing to their advantages, such as high efficiency, high energy density, quiet operation and environmental friendliness [1,2]. One of the key components for PEMFC is the proton exchange membrane (PEM), which separates the anode and the cathode compartment ideally allows for proton transport only. The current commercial PEM materials are perfluorosulfonated ionomer such as Nafion or Dow because of their good physical and chemical stability along with high proton conductivity under a wide range of relative humidity at moderate operation temperatures, but suffer from disadvantages such as limited operating temperature ($<80^\circ\text{C}$), high cost

and high methanol permeability. Consequently, much progress has been made to develop novel aromatic hydrocarbon polymers as alternative PEM materials and a number of sulfonated aromatic polymer such as poly(arylene ether)s, polyimides and polybenzimidazole have been developed as capable candidates [3,4]. Many hydrocarbon polymers show sufficiently high conductivity at high ion exchange capacities (IEC), which causes extensive water absorption above the critical temperature, or a dramatic loss of mechanical properties due to large dimensional swelling that render them unsuitable for practical PEM applications [5,6]. The dimensional stability and proton conductivity of aromatic hydrocarbon ionomer are crucial issues on improvement through the design of polymer structure. One promising approach to improve the properties and performance of aromatic hydrocarbon PEM is to induce distinct phase separation between the hydrophilic sulfonic acid containing regions and the hydrophobic polymer main chain by positioning the sulfonic acid groups on the end of side chains separately from the polymer main chain [7–9]. Currently, several research groups are focusing on the development of

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aliphatic side chain type sulfonated hydrocarbon-based polymers and methods to perform this strategy have been reported. Guiver and co-workers [10,11] reported a series of side chain type sulfonated poly(arylene ether sulfone)s by attaching pendant sulfonated aliphatic side chains to the backbone. The results also indicated that these side chain type sulfonated polymers exhibited very low water uptake and dimensional change, even at elevated temperatures (80 °C). Jannasch and co-workers reported a sulfoalkylated polysulfones that was prepared by attaching pendant sulfonated aliphatic side chains to polysulfone, showing proton conductivities of 0.07 S cm^{-1} at 70 °C [12]. Na and co-workers reported sulfonated aromatic polymers containing one or two pendant sulfoalkyl groups in each hydrophilic unit [13]. The highest conductivity of 0.102 S cm^{-1} was obtained in these copolymers ($\text{IEC} = 1.71 \text{ meq. g}^{-1}$) in a hydrated state at 80 °C, which have a low swelling ratio of 13.86%. In our previous work, we reported a series of poly(arylene ether sulfone)s by attaching pendant sulfonated side chains to the backbone [14,15]. These results also indicated that these side chain type sulfonated polymers possess advantageous proton conductivities and good dimensional stability.

In this paper, we reported on the synthesis of poly(arylene ether)s with two sulfonic acid groups on the end of an aliphatic side chain by disulfonated monomer and other commercial monomers. Selected PEM properties such as thermal and chemical stabilities, mechanical strength, water uptake behavior, proton conductivity and morphology were investigated in detail.

2. Experimental

2.1. Materials

All of the chemicals are reagent grade and purified by standard methods. 4-Phenylphenol, 2,6-difluorobenzoyl chloride and 3-phenylpropyl bromide were purchased from Sigma–Aldrich chemical corporation. 4,4'-Difluorobenzophenone (DFDPK) and 4,4'-(hexafluoroisopropylidene) diphenol (6FBPA) were purchased from TCI chemical company. The other solvents and catalysts were both ordered from Beijing Chemical Reagent Company.

2.2. Synthesis of monomer

(4-(3-Bromopropyl)phenyl)(2,6-difluorephenyl)methanone (A) was synthesized according to a procedure described as previous reported [14].

$^1\text{H NMR}$ (500 MHz, CDCl_3 , δ , ppm): 2.19 (q, 2H); 2.87 (t, 2H); 3.4 (t, 2H); 7.00 (t, 2H); 7.32 (d, 2H); 7.45 (m, 1H); 7.81 (d, 2H).

(4-(3-(4-Phenylphenoxy)propyl)phenyl)(2,6-difluorophenyl)methanone (B): a dry 250 mL three-necked round-bottomed flask equipped with a reflux condenser, mechanical stirrer and inlet of argon was charged with A (16.96 g, 0.05 mol), 4-phenylphenol (8.50 g, 0.05 mol), KOH (2.80 g, 0.05 mol), ethanol (50 mL). The reaction was complete after 4 h refluxing under argon protection (Scheme 1). The resulting mixture was cooled to room temperature, and then poured into 200 mL of water to give a white powdery

precipitate, which was collected by filtration. The crude product was purified by recrystallization from ethanol to obtain 20.8 g monomer B (yield 97%).

MP: 106.0 °C (by DSC).

MALDI-TOF MS (m/z): 429 $[\text{M} + \text{H}]^+$, 451 $[\text{M} + \text{Na}]^+$, 467 $[\text{M} + \text{K}]^+$.

$^1\text{H NMR}$ (500 MHz, $\text{DMSO}-d_6$, δ , ppm): 2.08 (m, 2H), 2.88 (t, 2H), 4.03 (t, 2H), 7.01 (d, 2H), 7.32 (d, 2H), 7.45 (m, 3H), 7.59 (q, 2H), 7.68 (m, 1H), 7.76 (d, 2H).

2.3. Synthesis of copolymers

A typical polycondensation procedure, illustrated by preparation of P-50 copolymer (where 50 is a molar percentage of monomer B in total difluoride monomer), was described as follows (Scheme 2). Into a 50 mL, three-necked, round-bottomed flask, fitted with a Dean–Stark trap, a reflux condenser, argon inlet, and a mechanical stirrer, were placed B (1.0712 g, 0.0025 mol), 4,4'-difluorobenzophenone (0.5455 g, 0.0025 mol), 4,4'-(hexafluoroisopropylidene)diphenol (1.6812 g, 0.005 mol), K_2CO_3 (0.76 g, 0.0055 mol), sulfolane (10 mL) and toluene (3 mL). The reaction mixture was refluxed for 3 h at 140–160 °C. After the produced water was removed by using toluene/water azeotrope, the reaction mixture was heated at 220 °C for about 3 h until a highly viscous solution was obtained. After the reaction mixture was cooled, it was poured into 100 mL of deionized water to obtain a white fibrous precipitate of polymer. The resulting polymer was filtered off and washed with hot water and hot methanol for several times. After vacuum drying at 120 °C for 12 h, P-50 copolymers were obtained.

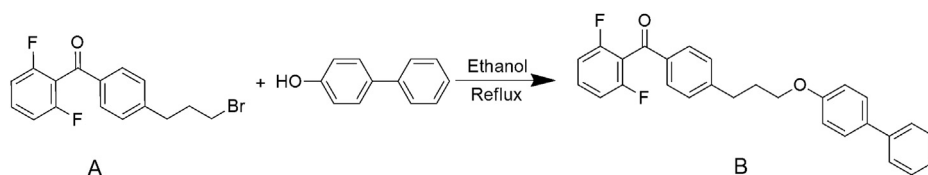
2.4. Sulfonation of copolymer

Polymers P-40 or P-50 reacted with chlorosulfonic acid in CH_2Cl_2 to obtain the sulfonated polymers I-40 or I-50. A typical sulfonation procedure follows (Scheme 2). A solution of chlorosulfonic acid (0.6 mL) in dichloromethane (20 mL) was placed in a round-bottomed flask. A solution of polymer P-40 or P-50 (1 g) in dichloromethane (30 mL) was added dropwise to the solution of chlorosulfonic acid in dichloromethane with stirring. The sulfonation reaction was allowed to proceed for 5 h until all of the sulfonated polymers had precipitated from the reaction mixture. The product was poured into hexane (100 mL) and filtered. The isolated polymers (I-40 or I-50) were washed with KOH aqueous solution and deionized water several times before being dried under vacuum at 120 °C overnight.

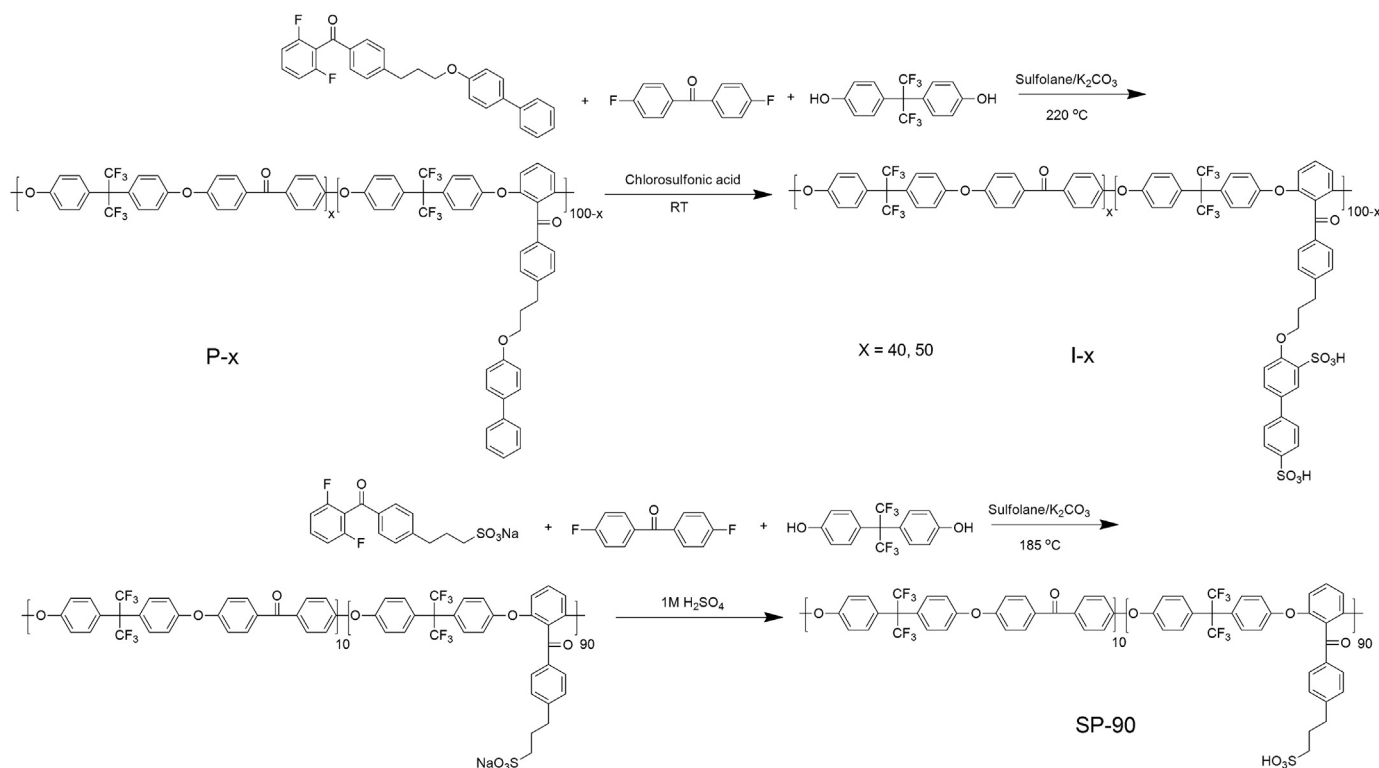
2.5. Synthesis of sulfonated copolymer SP-90

As corresponding polymer SP-90 with comparable IEC value to I-x was selected and synthesized according to a procedure described as previous reported [14].

$^1\text{H NMR}$ (500 MHz, $\text{DMSO}-d_6$, δ , ppm): 1.81 (m, 1.8H), 2.46 (t, 1.8H), 2.71 (t, 1.8H), 6.95 (d, 1.8H), 7.10 (d, 3.6H), 7.18–7.50 (m, 6.6H), 7.55 (m, 0.9H), 7.75 (d, 1.8H), 7.83 (d, 0.4H).



Scheme 1. Synthesis of difluoride monomer.



2.6. Preparation of sulfonated polymer membrane

The membrane was prepared by casting from a 10 wt% sulfonated copolymer solution in DMAc onto glass plate after filtration. The removal of DMAc was accomplished by drying at 80 °C for 10 h and then at 120 °C under vacuum for 12 h. After cooling, these membranes were immersed in deionized water and then peeled off. The acidification of the membranes was performed by immersing the membranes in 1 M H₂SO₄ at 90 °C for 2 h and then in deionized water at 100 °C for 5 h to remove the residual acid. The dry acid-form membranes in the controlled thickness range of 70–90 μm were obtained by drying at 120 °C for 12 h under vacuum.

2.7. Measurements

¹H NMR spectra were measured on a Bruker 510 spectrometer (500 MHz for ¹H) using CDCl₃ and DMSO-*d*₆ as solvents. Tetramethylsilane (TMS) was used as an internal standard. Differential scanning calorimeter (DSC) measurements were performed on a Mettler Toledo DSC821^e instrument. Thermogravimetric analysis (TGA) was performed to assess thermal stability of membranes with Pyris 1 TGA (Perkin–Elmer) under a nitrogen atmosphere. Before analysis, the films were dried and kept in the TGA furnace at 120 °C in a nitrogen atmosphere for 30 min. The samples were cooled to 80 °C and then reheated to 800 °C at 10 °C min^{−1}, and the temperatures at 5% and 10% weight loss were recorded for each sample.

2.7.1. Water uptake and swelling ratio measurements

The water uptake and swelling ratio were determined by measuring the difference in the weight and length between the completely dried and hydrated membranes, respectively. A piece of acid-form film (1 cm × 5 cm × ~60 μm) was dried at 100 °C under vacuum to a constant weight, which was recorded as *W*_{dry} and then immersed into deionized water at desired temperatures for 4 h.

During this period, the wet membrane was quickly weighed several times after wiping off the water on the surface with tissue paper until a constant weight was obtained, which was recorded as *W*_{wet}. The water uptake of the membranes were calculated from the change of film weight by the following equation:

$$\text{Water uptake (\%)} = \left[\frac{(W_{\text{wet}} - W_{\text{dry}})}{W_{\text{dry}}} \right] \times 100\%$$

The swelling ratio was calculated from the change of film length by:

$$\text{Swelling ratio (\%)} = \left[\frac{(L_{\text{wet}} - L_{\text{dry}})}{L_{\text{dry}}} \right] \times 100\%$$

where *L*_{wet} and *L*_{dry} are the lengths of the wet and dry membranes, respectively.

2.7.2. Proton conductivity

The proton conductivity of these membranes was measured on a Solatron 1260/1287 impedance analyzer by a four-electrode ac impedance method over a frequency range of 10–10⁶ Hz with 50–500 mV oscillating voltage. A sheet of the sulfonated membrane (3 cm × 1 cm) was washed with ultrapure water and placed in a test cell. Before the measurements, the membranes were fully hydrated in ultrapure water at different temperatures for 48 h. Conductivity measurements of fully hydrated membranes were carried out with the cell immersed in liquid water at the desired temperature, which ranged from 20 to 80 °C. The conductivity (σ) of the membranes in the transverse direction was calculated from the following equation:

$$\sigma = D/RA$$

where *D* is the distance between the two electrodes. *R* and *A* are the measured resistance and transverse area of the film samples, respectively.

2.7.3. Mechanical properties of membranes

The mechanical properties of wet membranes were measured at room temperature on SHIMADIU AG-I 1 KN at a strain rate of 2 mm min^{-1} . The samples ($20 \text{ mm} \times 4 \text{ mm}$) in wet state were obtained by immersing them in water at room temperature for more than 48 h.

2.7.4. Morphological analysis

Small angle X-ray scattering (SAXS, Rigaku D/max-2550) was measured for membranes at 50% RH and room temperature. The membranes were enveloped in a Mylar bag and irradiated by X-ray ($\text{CuK}\alpha$, $\lambda_i = 1.54 \text{ \AA}$) with 40 kV. The range of scattering vectors explored ($q = 4\pi\sin 2\theta/\lambda_i$) was from 0.085 to 3.0 nm^{-1} , where λ_i and 2θ are the incident wavelength and total scattering angle, respectively. The characteristic separation length (d), i.e. the Bragg spacing, was calculated as: $d = 2\pi/q$.

2.7.5. Ion exchange capacity (IEC)

Ion exchange capacity (IEC) of these proton exchange membranes was measured by classical titration. The membranes in acid form were accurately weighed and immersed in 25 mL , 1 mol L^{-1} NaCl solution for 48 h at room temperature for the replacement Na^+ with H^+ . Released protons were titrated using NaOH solution.

3. Results and discussions

3.1. Synthesis of monomer

The two-step synthetic route for the difluoride monomer (B) is shown in Scheme 1. Monomer A was first prepared by an aluminum chloride anhydrous-catalyzed Friedel–Crafts acylation of 3-phenylpropyl bromide with 2,6-difluorobenzoyl chloride and subsequently reacted with 4-phenylphenol by Williamson reaction. The structure of B was confirmed by ^1H NMR spectroscopy and MALDI-TOF MS. As shown in Fig. 1, all ^1H NMR signal peaks were well assigned, three signal peaks at 1.9 – 4.0 ppm are assigned to aliphatic protons, and multiples signal at 6.9 – 7.8 ppm are assigned to aromatic protons. Furthermore, the formula weight of B was confirmed by MALDI-TOF MS. As a result, the expected monomer was obtained.

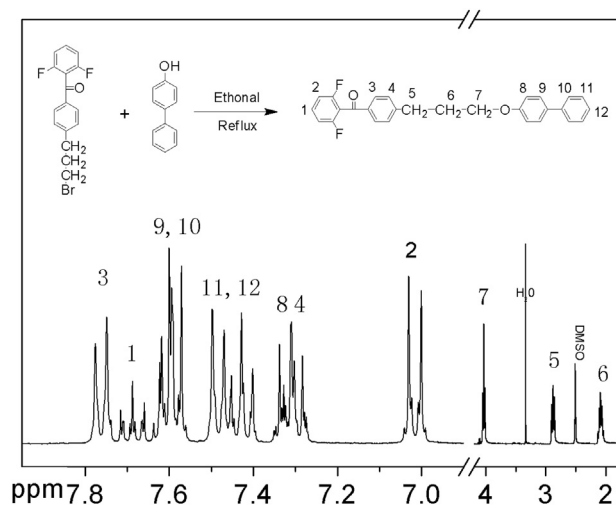


Fig. 1. The ^1H NMR spectrum of difluoride monomer.

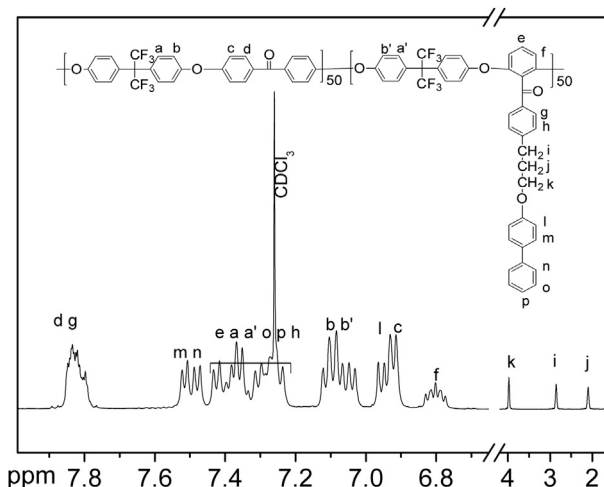


Fig. 2. The ^1H NMR spectrum of P-50 copolymers.

3.2. Synthesis and sulfonation of copolymer

Poly(arylene ether) copolymers P-40 and P-50 were prepared by polycondensation of 6FBPA, DFDPK, and B, as indicated in Scheme 2. They were denoted as P-x, where “x” is the molar percentage of B in the feed. Obtained polymers were readily soluble in conventional solvent such as DMAc, DMSO, NMP, and chloroform. The structures were confirmed by ^1H NMR analyses, as shown in Fig. 2, in which all signals were well assigned and expected structures of copolymers were confirmed.

The obtained P-x were sulfonated using chlorosulfonic acid in dichloromethane at room temperature to give I-x. I-40 and I-50 copolymer containing different contents of monomer B, which can afford expected sulfonation position on electron-rich pendant phenyl ring. 6FBPA and DFDPK were selected as the other two monomers in the copolymerization, since polymer main chain with the structure of poly(arylene ether ketone)s containing fluorine takes excellent stability under the sulfonation condition so that neither sulfonation nor chain cleavage occurred on the phenyl rings in the main chain [16,17]. Therefore, the sulfonic acid groups can be introduced separately on the pendant phenyls in the side chain. In order to achieve complete sulfonated of P-x, an excess amount chlorosulfonic acid was used. After sulfonation, a part of the

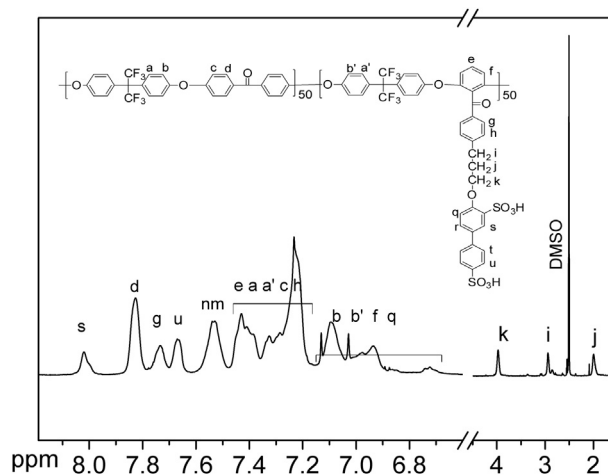


Fig. 3. The ^1H NMR spectrum of I-50 copolymers.

Table 1

IEC values, inherent viscosity, thermal and mechanical properties of I-x, SP-90 and Nafion 117.

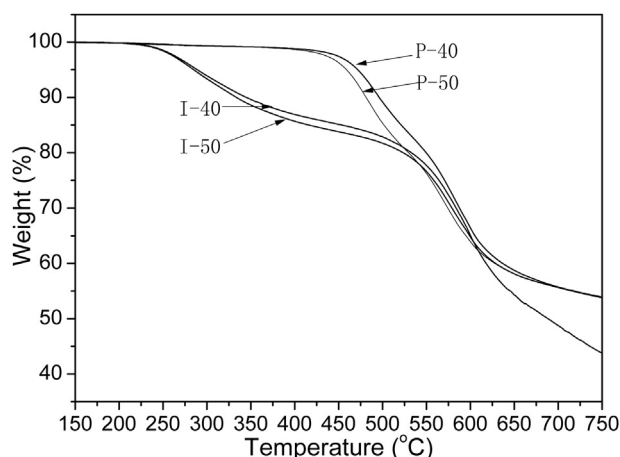
Polymer	IEC ^a (meq. g ⁻¹)	IEC ^b (meq. g ⁻¹)	η_{inh} ^c (dL g ⁻¹)	T_{donset} (°C)	Tensile strength (MPa)	Elongation at break (%)
I-40	1.20	1.15	1.22	249	29	35
I-50	1.43	1.32	1.37	241	31	24
SP-90	1.39	1.37	0.90	217	41	26
Nafion117	0.91	—	—	—	27	327

^a The theoretical IEC value.^b The experimental IEC values of the I-x were determined by classical titration, using NaOH aqueous solution and phenolphthalein as an indicator.^c Inherent viscosity of polymers.

sulfonic acid groups existed as sulfonyl chlorides because of the excess chlorosulfonic acid. Therefore, all sulfonyl chloride groups were hydrolyzed in KOH aqueous solution. The sulfonated polymer exhibited good solubility in polar aprotic solvents such as DMF, DMAc, NMP, and DMSO. Tough, flexible, and transparent membranes of I-x were obtained by solution casting. The structure of I-x was confirmed by FT-IR and ¹H NMR spectroscopy. The characteristic sulfonic acid absorption was observed at 1030 cm⁻¹ in IR spectrum. The ¹H NMR spectrum of I-50 is shown in Fig. 3. In comparison with the spectrum of the precursor copolymer P-50, new signals appeared at about 8.05 and 7.65 ppm were assigned to the g and u protons, which were in the neighborhood of the electron-drawing sulfonic acid groups. As a result, the desired polymer was obtained. Inherent viscosities of I-40 and I-50 in DMAc at 25 °C are 1.22 and 1.37 dL g⁻¹, respectively, indicating their high molecular weights. In order to improve the overall properties of I-x, the appropriate IEC value (1.2–1.5 meq. g⁻¹) was designed. As seen in Table 1, the experimental IEC values of I-x, which were determined by titration agreed well with theoretical values.

3.3. Thermal stability

The thermal stability of P-x and I-x membranes were evaluated by TGA under nitrogen. Prior to the measurement, the hygroscopic samples were preheated at 120 °C for 30 min to remove any absorbed moisture. As shown in Fig. 4, the onset weight loss temperature of unsulfonated copolymer P-40 and P-50 is higher than 450 °C, which indicates their good thermal stability. And both sulfonated samples with higher onset weight loss temperature ($T_{donset} > 240$ °C, Table 1) displayed a two-stage weight loss behavior. The initial degradation step in the range of 241–400 °C is

**Fig. 4.** The TGA curves of copolymers.**Table 2**

Water uptake, swelling ratio, proton conductivity, activation energy of I-x, SP-90 and Nafion 117.

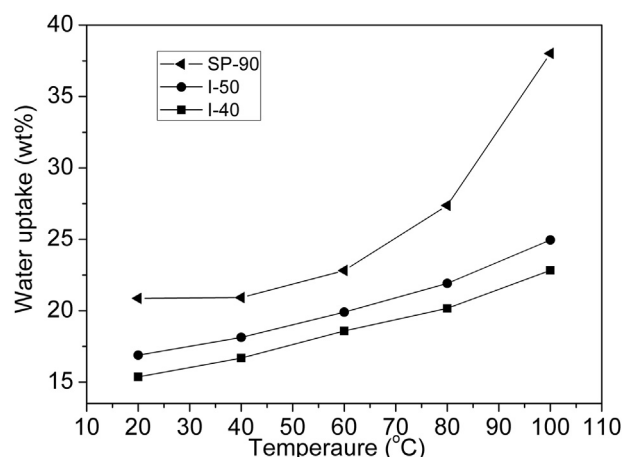
Polymer	WU ^a (wt%)	SR ^b (L%)		σ (mS cm ⁻¹)	E_a (kJ mol ⁻¹)
		X ^b	Z ^c		
I-40	20.1	7.4	17.0	90	11.00
I-50	21.9	8.1	26.5	105	10.67
SP-90	27.4	9.7	36.5	69	19.35
Nafion117 [14]	29.4	20.2	22	108	9.7

^a Measured in 80 °C.^b In-plane (length) swelling ratio.^c Through-plane (thickness) swelling ratio.

ascribed to the dehydration between the sulfonic acids and desulfonation reaction and the weight losses of sulfonic acid groups were in proportion to the various IEC values. The second stage weight losses starting from 400 °C are attributed to the decomposition of the polymer side chains and main chains, respectively.

3.4. Water uptake and swelling ratio

As shown in Table 2, I-x membranes with IEC of 1.15 and 1.32 meq. g⁻¹ exhibited appropriate water uptake, which are 20.1% and 21.9% at 80 °C, respectively. As shown in Fig. 5, I-x membranes have lower water uptake than that of SP-90 in all range of test temperatures. In addition, compared to SP-90, a sharp increase water absorption was not observed after 80 °C in I-40 or I-50, which benefit from their morphological stability. The swelling ratio of I-40, I-50, SP-90 and Nafion 117 were obtained in both in-plane and through-plane direction. All of the I-x membranes exhibited a lower in-plane swelling ratio than that of Nafion 117 at 80 °C (Table 2). The side chain type PEM I-x and SP-90 membranes showed generally a lower in-plane swelling ratio than many main-chain type sulfonated poly(arylene ether)s at similar IEC level [7]. But I-x membranes showed anisotropic swelling behavior and through-plane swelling ratio are higher than that of Nafion 117. I-x membranes take lower volume swelling ratio than Nafion 117, which is an important factor of membrane electrode assembly (MEA). Compared with main-chain type SPAE, the side chain type SPAE bearing flexible side chain between the sulfonic acid and main chain may be more effective in suppressing the swelling behavior of the films by inducing hydrophobic and hydrophilic domain phase separation [18]. In addition, compared with single sulfonated side chain type SP-90, the disulfonated side chain type I-x membranes

**Fig. 5.** The water uptake of sulfonated polymers as a function of temperature.

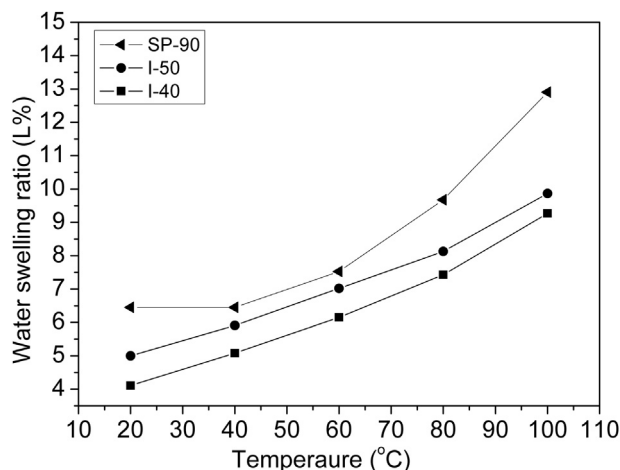


Fig. 6. The swelling ratio of sulfonated polymers as a function of temperature.

exhibited lower swelling ratio at a function of temperature (Fig. 6). This may be due to their longer hydrophobic moiety and higher density flexible sulfonated side group.

3.5. Proton conductivity

Proton conductivities of the I-x, SP-90, and Nafion 117 membranes were measured in water as a function of temperature. As seen in Table 2, an outstanding result was observed. I-50 with very low swelling ratio exhibited proton conductivity of 105 mS cm^{-1} which is comparable with Nafion 117 (108 mS cm^{-1}), and higher than that of SP-90 with the similar level of IEC at 80°C . Fig. 7 shows the proton conductivities of those PEMs as a function of temperature. The proton conductivity of I-x membranes reveals a trend towards similarly to the increasing IEC and temperature, and is higher than that of SP-90 at a range of test temperature. The proton transfer barriering property of proton through the membranes as reflected by activation energy (E_a) is calculated using Arrhenius equation from the slope in Fig. 7. As can be seen from the Arrhenius plots in Fig. 7, I-40 and I-50 show a similar activation energy of about 11 kJ mol^{-1} . The value of activation energy is higher than that of Nafion 117, but lower than the membranes which we reported before (SP-90). The reduced E_a and enhanced proton conductivity

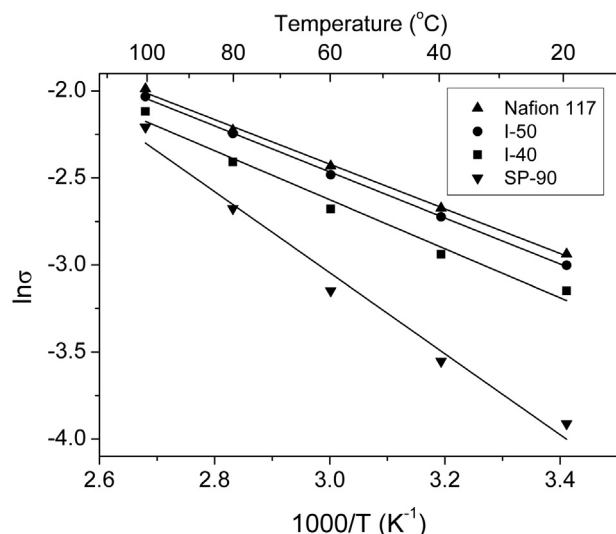


Fig. 7. Arrhenius plot of proton conductivity as a function of temperature.

further proved the effect of the formed ionic clusters, which interconnect the proton channels via $-\text{SO}_3\text{H}$ groups. For the I-x copolymers, the incorporation of cluster of flexible side chain sulfonic acid groups could be beneficial to aggregate the ionic clusters, which would lead to a more pronounced separation into hydrophilic/hydrophobic domains and improve proton conductivity. The proton conductivities of those membranes are all higher than $10^{-2} \text{ S cm}^{-1}$, especially, I-x membrane is very close to that of Nafion 117 at room temperature, indicating they are suitable for the application in PEMFC. Random aromatic sulfonated PEMs generally require relatively high IEC values to attain high proton conductivity because of lower acidity and chain flexibility of sulfonic acid groups which leads to poor hydrophilic/hydrophobic micro phase separation compared to Nafion [5].

3.6. Morphology and mechanical properties

The ability of the sulfonated polymers to form ionic clusters was studied by SAXS, a method which allows an identification of the characteristic separation length between the ionic domains in terms of the position (q -value) and width of the so-called ionomer peak. The SAXS profiles of I-40, SP-90, and Nafion 117 are shown in Fig. 8. Prior to the scattering experiments, the membranes were ion-exchanged to the Pb^{2+} form to increase the contrast between the ionic clusters and the hydrophobic polymer-rich matrix phase [19]. As seen in Fig. 8, the ionomer peak of Nafion 117 appeared at $q = 1.99 \text{ nm}^{-1}$, implying its distinct ionic clusters with a characteristic separation length of $d = 3.16 \text{ nm}$. The sharp ionomer peak of I-40 membranes was shifted to lower q -values 1.09 nm^{-1} with a characteristic separation length of $d = 5.76 \text{ nm}$, indicating its larger separation lengths between the ionic clusters, as compared to the profile of Nafion 117. At similar IEC level, the I-40 exhibited lower ionomer peak and larger separation length in comparison with corresponding SP-90 with $q = 1.91 \text{ nm}^{-1}$ and $d = 3.28 \text{ nm}$, which demonstrated a larger separation lengths in former membrane attributed to the disulfonated pendant group. It is also confirmed by the results that I-x PEM have better performance than SP-90, such as dimensional stability and proton conductivity.

As seen in Table 1, the I-x membranes in environments with relative humidity of 40% and RT exhibited elongations at break of 35–24%, and tensile strength of 29–31 MPa. Those results indicate I-x membranes were sufficiently tough and ductile for potential use as PEM materials.

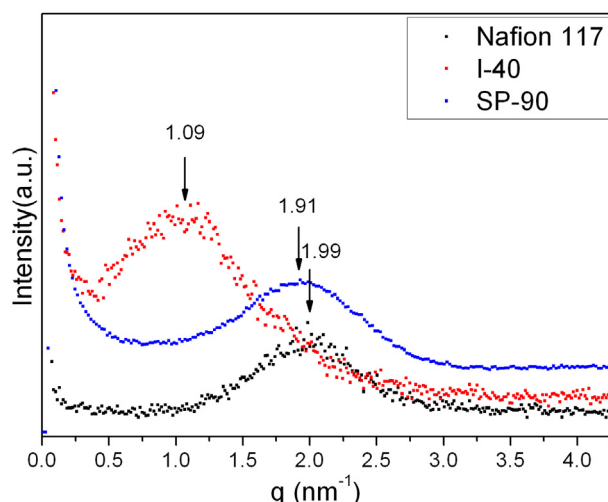


Fig. 8. The SAXS profile of sulfonated copolymers and Nafion 117.

4. Conclusion

A novel difluoride monomer with aliphatic pendant was successfully synthesized. Based on this monomer, aliphatic side chain containing disulfonated poly(arylene ether)s (I-x) was obtained via classic polycondensation reaction and subsequently sulfonation procedure. Introducing flexible aliphatic group between hydrophobic main chain and hydrophilic disulfonated pendant which effectively improved a balanced relationship of proton conductivity and swelling for I-x. The I-50 membrane exhibited comparable proton conductivity to Nafion 117 and lower swelling ratio less than 10% at 100 °C. In addition, compared to single sulfonic acid side chain type SP-90 with similar IEC value, I-x have higher proton conductivity and lower swelling ratio. The suitable properties were attributed to their special molecular structure and better morphology. Combined proton conductivity, water swelling data, and mechanical properties suggest that I-x membranes have the properties most suitable for PEM application.

Acknowledgements

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